

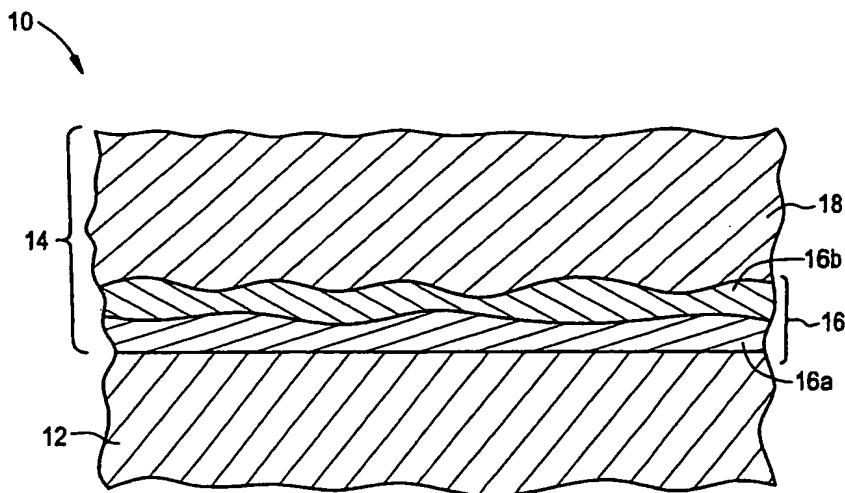
PCT

WORLD INTELLECTUAL PROPERTY ORGANIZATION
International Bureau

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : C23C 4/02, 28/00	A1	(11) International Publication Number: WO 99/43861 (43) International Publication Date: 2 September 1999 (02.09.99)
(21) International Application Number: PCT/US99/04339 (22) International Filing Date: 26 February 1999 (26.02.99) (30) Priority Data: 60/076,391 28 February 1998 (28.02.98) US 09/259,649 26 February 1999 (26.02.99) US (71) Applicant: GENERAL ELECTRIC COMPANY [US/US]; 1 River Road, Schenectady, NY 12345 (US). (72) Inventor: ZHENG, Xiaoci; 11 Windsor, London Square Apartments, Clifton Park, NY 12065 (US). (74) Agents: WINTER, Catherine, J. et al.; General Electric Company, 3135 Easton Turnpike W3C, Fairfield, CT 06431 (US).	(81) Designated States: CZ, JP, KR, European patent (AT, BE, CH, CY, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE). Published <i>With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</i>	

(54) Title: MULTILAYER BOND COAT FOR A THERMAL BARRIER COATING SYSTEM AND PROCESS THEREFOR



(57) Abstract

A method of depositing a bond coat (16) of a thermal barrier coating (TBC) system (14) for components designed for use in a hostile thermal environment, such as turbine, combustor and augmentor components (10) of a gas turbine engine. The method yields a dense, bi-layer bond coat (16) having an adequate surface roughness for adhering a plasma-sprayed ceramic layer (18). The method generally entails depositing a first bond coat layer (16a) using a high velocity oxy-fuel (HVOF) technique employing a relatively fine metallic powder having a relatively narrow size distribution. Following heat treatment, a second bond coat layer (16b) is deposited on the first bond coat layer (16a) by air plasma spraying (APS) a relatively coarser metallic powder of particles having a relatively broader size distribution. The resulting second bond coat layer (16b) is characterized by a macro-surface roughness of about 450 to about 750 microinches Ra. Following a second heat treatment, the ceramic layer (18) is deposited that adheres to the bond coat (16) through mechanical interlocking with the rough surface of the second coat layer (16b).

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AL	Albania	ES	Spain	LS	Lesotho	SI	Slovenia
AM	Armenia	FI	Finland	LT	Lithuania	SK	Slovakia
AT	Austria	FR	France	LU	Luxembourg	SN	Senegal
AU	Australia	GA	Gabon	LV	Latvia	SZ	Swaziland
AZ	Azerbaijan	GB	United Kingdom	MC	Monaco	TD	Chad
BA	Bosnia and Herzegovina	GE	Georgia	MD	Republic of Moldova	TG	Togo
BB	Barbados	GH	Ghana	MG	Madagascar	TJ	Tajikistan
BE	Belgium	GN	Guinea	MK	The former Yugoslav Republic of Macedonia	TM	Turkmenistan
BF	Burkina Faso	GR	Greece	ML	Mali	TR	Turkey
BG	Bulgaria	HU	Hungary	MN	Mongolia	TT	Trinidad and Tobago
BJ	Benin	IE	Ireland	MR	Mauritania	UA	Ukraine
BR	Brazil	IL	Israel	MW	Malawi	UG	Uganda
BY	Belarus	IS	Iceland	MX	Mexico	US	United States of America
CA	Canada	IT	Italy	NE	Niger	UZ	Uzbekistan
CF	Central African Republic	JP	Japan	NL	Netherlands	VN	Viet Nam
CG	Congo	KE	Kenya	NO	Norway	YU	Yugoslavia
CH	Switzerland	KG	Kyrgyzstan	NZ	New Zealand	ZW	Zimbabwe
CI	Côte d'Ivoire	KP	Democratic People's Republic of Korea	PL	Poland		
CM	Cameroon	KR	Republic of Korea	PT	Portugal		
CN	China	KZ	Kazakstan	RO	Romania		
CU	Cuba	LC	Saint Lucia	RU	Russian Federation		
CZ	Czech Republic	LI	Liechtenstein	SD	Sudan		
DE	Germany	LK	Sri Lanka	SE	Sweden		
DK	Denmark	LR	Liberia	SG	Singapore		
EE	Estonia						

- 1 -

MULTILAYER BOND COAT FOR A
THERMAL BARRIER COATING SYSTEM
AND PROCESS THEREFOR

5

BACKGROUND OF THE INVENTION

The present invention relates to protective coatings for components exposed to high temperatures, such as components of a gas turbine engine. More particularly, this invention is directed to a process for forming a bond coat of a thermal barrier coating system, and specifically a dense multilayer bond coat having a desirable level of surface roughness to promote mechanical interlocking between the bond coat and a thermal barrier coating deposited on the bond coat.

The operating environment within a gas turbine engine is both thermally and chemically hostile. Significant advances in high temperature alloys have been achieved through the formulation of iron, nickel and cobalt-base superalloys though components formed from such alloys often cannot withstand long service exposures if located in certain high-temperature sections of a gas turbine engine, such as the turbine, combustor or augmentor. Examples of such components include buckets and nozzles in the turbine section of a gas turbine engine. A common solution is to protect the surfaces of such components with an environmental coating system, such as an aluminide coating, an overlay coating or a thermal barrier coating (TBC) system. The latter includes a layer of thermal-insulating ceramic (thermal barrier coating, or TBC) adhered to the superalloy substrate with an environmentally-resistant bond coat.

Metal oxides, such as zirconia (ZrO_2) that is partially or fully stabilized by yttria (Y_2O_3), magnesia (MgO) or another oxide, have been widely employed as the material for the thermal-insulating ceramic layer. The ceramic layer is typically deposited by air plasma spray (APS), vacuum plasma spray (VPS) (also called low pressure

- 2 -

plasma spray (LPPS)), or a physical vapor deposition (PVD) technique, such as electron beam physical vapor deposition (EBPVD) which yields a strain-tolerant columnar grain structure. APS is often preferred over other deposition processes because of low equipment cost and ease of application and masking. Notably, the adhesion mechanism for plasma-sprayed ceramic layers is by mechanical interlocking with a bond coat having a relatively rough surface, preferably about 350 microinches to about 750 microinches (about 9 to about 19 μ m) Ra.

Bond coats are typically formed from an oxidation-resistant alloy such as MCrAlY where M is iron, cobalt and/or nickel, or from a diffusion aluminide or platinum aluminide that forms an oxidation-resistant intermetallic, or a combination of both. Bond coats formed from such compositions protect the underlying superalloy substrate by forming an oxidation barrier for the underlying superalloy substrate. In particular, the aluminum content of these bond coat materials provides for the slow growth of a dense adherent aluminum oxide layer (alumina scale) at elevated temperatures. This oxide scale protects the bond coat from oxidation and enhances bonding between the ceramic layer and bond coat.

Aside from those formed by diffusion techniques and physical or chemical vapor deposition, bond coats are typically applied by thermal spraying, e.g., APS, VPS and high velocity oxy-fuel (HVOF) techniques, all of which entail deposition of the bond coat from a metal powder. The structure and physical properties of such bond coats are highly dependent on the process and equipment by which they are deposited. Little oxidation of the metal particles occurs during deposition by VPS methods, such that the resulting bond coats are dense and free of oxides, and therefore are protective at high temperatures (e.g., above 1000 C (about 1800 F)) because of their ability to grow a continuous protective oxide scale. Because of a relatively low heat capacity to melt the spray powder, VPS processes typically employ powders having a very fine particle size distribution, with the result that as-sprayed VPS bond coats are dense but have relatively smooth surfaces (typically 200 to 350 microinches (about 4 to

- 3 -

about 9 μ m)) Ra. Consequently, plasma-sprayed ceramic layers do not adhere well to VPS bond coats.

In contrast, air plasma possesses a higher heat capacity in the presence of air. The higher heat capacity of the APS process
5 enables the melting of relatively large particles, permitting the use of metal powders that yield bond coats having a rougher surface than is possible with VPS. The adhesion of a ceramic layer to an APS bond coat is enhanced by the rough APS bond coat surface, e.g., in the 350 to 750 microinch (about 9 to about 19 μ m) Ra range suitable for
10 plasma-sprayed ceramic layers. The particle size distribution of such powders is Gaussian as a result of the sieving process, and is typically broad in order to provide finer particles that fill the interstices between larger particles to reduce porosity. However, the finer particles are prone to oxidation during the spraying process, resulting in a bond coat
15 having a very high oxide content. The low momentum possessed by the sprayed particles in the APS process also promotes porosity in the coating. Consequently, as-sprayed APS bond coats inherently contain relatively high levels of oxides and are more porous than are VPS bond coats, for example, exhibiting densities of greater than 95% of
20 theoretical. Because of their higher level of oxides and porosity, APS bond coats are more prone to oxidation than are VPS bond coats.

Bond coats deposited by HVOF techniques are very sensitive to particle size distribution of the powder because of the relatively low spray temperature of the HVOF process. Accordingly,
25 HVOF process parameters are adjusted to spray powders having a very narrow range of particle size distribution. To produce a bond coat having a surface roughness of at least 350 microinches Ra, a coarse powder must be used in an HVOF process. However, because coarse particles cannot typically be fully melted at suitable HVOF parameters, the resulting bond coat typically exhibits relatively high porosity and
30 poor bonding between sprayed particles. To produce a more dense bond coat using a HVOF process, a finer powder must typically be used, with the result that a thermal barrier coating does not adhere well

- 4 -

to the bond coat due to the bond coat lacking surface features that provide micro-roughness.

In view of the above, it can be seen that, while bond coats deposited by various techniques have been successfully employed, each has advantages and disadvantages that must be considered for a given application. In particular, while APS processes readily yield a bond coat having adequate surface roughness to adhere a plasma-sprayed ceramic layer, porosity and the tendency for oxidation in such bond coats are drawbacks to the protection and adhesion they provide to the underlying substrate. Accordingly, what is needed is a process by which the surface roughness necessary for a plasma-sprayed ceramic layer can be achieved for a bond coat while also achieving reduced porosity and oxidation.

SUMMARY OF THE INVENTION

According to the present invention, there is provided a bond coat of a thermal barrier coating (TBC) system for components designed for use in a hostile thermal environment, such as turbine buckets and nozzles, combustor components, and augmentor components of a gas turbine engine. Also provided is a method of depositing the bond coat, which produces an adequate surface roughness for adhering a plasma-sprayed ceramic layer while also producing a bond coat that is sufficiently dense to inhibit diffusion of oxygen and other oxidizing agents to the component substrate. Consequently, bond coats produced by the method of this invention are protective and yield thermal barrier coating systems that are highly resistant to spallation.

The method generally entails forming a bond coat by depositing a first bond coat layer on a suitable substrate using a HVOF technique employing a first metallic powder having a maximum particle size of 55 micrometers, a suitable range being about 20 to 55 m. The resulting bond coat layer has a surface roughness of about 200 to about 450 microinches (about 5 to about 11 m) Ra. Prior to exposure to a high-temperature oxidizing environment, the first bond coat layer is

- 5 -

heat treated in a vacuum or inert atmosphere to densify the first bond coat layer and diffusion bond the particles. A second bond coat layer is then deposited on the first bond coat layer by air plasma spraying a second metallic powder of particles having a size of from about 35 to about 110 micrometers. The particles are deposited to cause the second bond coat layer to have a porosity of less than 5% of theoretical density and a macro-surface roughness of about 450 to about 750 microinches (about 11 to about 19 m) Ra. Prior to exposure to a high-temperature oxidizing environment, the first and second bond coat layers are heat treated in a vacuum or inert atmosphere to diffusion bond the second bond coat layer to the first bond coat layer. Thereafter, a thermal-insulating ceramic layer can be deposited that adheres to the bond coat through mechanical interlocking with the rough surface of the second bond coat layer.

According to this invention, the surface roughness of the resulting bi-layer bond coat is attributable to particles of the second metallic powder being incompletely melted during deposition, yielding a macro-surface roughness of at least about 450 microinches Ra. The finer particles of the second metallic powder fill the interstices between the larger particles to a degree sufficient to achieve a density of at least about 95% of theoretical. The finer particles of the second metallic powder also contribute to the micro-surface roughness of the bond coat, which has been determined to greatly enhance the adhesion of the thermal barrier coating when combined with the macro-surface roughness provided by the coarser particles.

From the above, it can be seen that the method of this invention produces a low-porosity bond coat having a surface roughness necessary for a plasma-sprayed ceramic layer of a thermal barrier coating system. Accordingly, bond coats produced by the present invention are able to adhere plasma-sprayed ceramic layers, such that the thermal barrier coating system exhibits a desirable level of spallation resistance while inhibiting oxidation of the underlying substrate.

- 6 -

Other objects and advantages of this invention will be better appreciated from the following detailed description.

DESCRIPTION OF THE DRAWINGS

Figure 1 schematically represents a thermal barrier coating system having a bi-layer bond coat deposited in accordance with this invention.

DETAILED DESCRIPTION OF THE INVENTION

The present invention is generally applicable to metal components that are protected from a thermally and chemically hostile environment by a thermal barrier coating (TBC) system. Notable examples of such components include the high and low pressure turbine nozzles and blades, shrouds, combustor liners and augmentor hardware of gas turbine engines, and buckets of industrial turbine engines. While the advantages of this invention are particularly applicable to turbine engine components, the teachings of this invention are generally applicable to any component on which a thermal barrier may be used to thermally insulate the component from its environment.

A partial cross-section of a turbine engine component 10 having a thermal barrier coating system 14 in accordance with this invention is represented in Figure 1. The coating system 14 is shown as including a thermal-insulating ceramic layer 18 bonded to a substrate 12 with a bi-layer bond coat 16. As is the situation with high temperature components of a turbine engine, the substrate 12 may be formed of an iron, nickel or cobalt-base superalloy, though it is foreseeable that other high temperature materials could be used. According to this invention, the ceramic layer 18 is deposited by plasma spraying techniques, such as air plasma spraying (APS) and vacuum plasma spraying (VPS), the latter of which is also known as low pressure plasma spraying (LPPS). A preferred material for the ceramic layer 18 is an yttria-stabilized zirconia (YSZ), though other ceramic materials could be used, including yttria, partially stabilized

- 7 -

zirconia, or zirconia stabilized by other oxides, such as magnesia (MgO), ceria (CeO₂) or scandia (Sc₂O₃).

The bond coat 16 must be oxidation-resistant so as to protect the underlying substrate 12 from oxidation and to enable the plasma-sprayed ceramic layer 18 to more tenaciously adhere to the substrate 12. In addition, the bond coat 16 must be sufficiently dense to inhibit the diffusion of oxygen and other oxidizing agents to the substrate 12. Prior to or during deposition of the ceramic layer 18, an alumina (Al₂O₃) scale (not shown) may be formed on the surface of the bond coat 16 by exposure to elevated temperatures, providing a surface to which the ceramic layer 18 tenaciously adheres. For this purpose, the bond coat 16 preferably contains alumina- and/or chromia-formers, i.e., aluminum, chromium and their alloys and intermetallics. Preferred bond coat materials include MCrAl and MCrAlY, where M is iron, cobalt and/or nickel.

Finally, because the ceramic layer 18 is deposited by plasma spraying, the bond coat 16 must have a sufficiently rough surface, preferably at least 350 microinches (about 9 μ m) Ra in order to mechanically interlock the ceramic layer 18 to the bond coat 16. The present invention produces the bond coat 16 to have sufficient density and surface roughness by depositing a first bond coat layer 16a using a high velocity oxy-fuel (HVOF) process and a relatively fine powder having a relatively narrow particle size distribution, followed by a second bond coat layer 16b deposited by air plasma spraying (APS) and using a coarser powder having a relatively broader particle size distribution. Notably, prior art HVOF bond coats are typically either too smooth to adequately adhere a plasma-sprayed bond coat, or have adequate surface roughness but at the expense of lower coating density and poor integrity, while prior art APS bond coats can be deposited to have adequate surface roughness but undesirably high porosity, e.g., less than 95% of theoretical density. By combining the bond coat layers 16a and 16b produced by the processes and powders of this invention, the present invention provides a dense multilayer

- 8 -

bond coat 16 having desirable surface roughness, e.g., at least 350 microinches Ra.

As indicated above, the HVOF and APS processes of this invention require the use of two metal powders with different particle size distributions. At least the second bond coat layer 16b, and preferably both bond coat layers 16a and 16b, are formed of an oxide scale-forming metal composition, such as an aluminum-containing intermetallic, chromium-containing intermetallic, MCrAl, MCrAlY, or a combination thereof. A particularly suitable composition for both bond coat layers 16a and 16b has a nominal composition, in weight percent, of about 22% chromium, about 10% aluminum, about 1% yttrium, the balance nickel and incidental impurities. The HVOF bond coat layer 16a provides a very dense barrier to oxidation as a result of the fine powder having a narrow particle size distribution range, while the second layer 16b has a desirable micro-surface roughness and macro-surface roughness attributable to the finer and coarser particles, respectively, present in the powder used with the APS process. The resulting combination of micro- and macro-roughness has been found to promote the mechanical interlocking capability of the bond coat 16 with the subsequently-applied ceramic layer 18.

According to this invention, the powder for the HVOF process has a maximum particle size of about 55 m. A preferred particle size distribution is, in weight percent, about 19% particles from 44 to 55 m, about 42% particles from 31 to 44 m, about 31% particles from 22 to 31 m, and about 5% particles from 16 to 22 m. Preferred parameters include a spray rate of about three to eight pounds (about 1.4 to 3.6 kg) per hour, a spray distance of about five to twelve inches (about 0.13 to 0.30 meter), a fuel gas mixture of oxygen, hydrogen and nitrogen, and a maximum surface temperature of about 350 F (about 175 C).

The powder for the APS process preferably has a particle size range of about 35 to 110 m. A preferred particle size distribution is, in weight percent, about 5% particles from 75 to 90 m, about 25%

- 9 -

particles from 63 to 75 m, about 50% particles from 53 to 63 m, about 15% particles from 45 to 53 m, and about 5% particles from 38 to 45 m. Preferred parameters include a spray rate of about twenty to sixty grams per minute, a spray distance of about three to six inches (about 0.08 to 0.15 meter), and a current level of about 350 to 650 amps using a gas mixture of hydrogen and nitrogen.

According to this invention, a suitable thickness for the HVOF bond coat layer 16a is about 100 to about 300 micrometers. The HVOF process and powder described above produce a bond coat layer 16a having a surface roughness of about 200 to about 450 microinches (about 5 to about 11 m) Ra and a density of at least about 99% of theoretical. Prior to exposure to a high-temperature oxidizing environment, the bond coat layer 16a is heat treated to diffusion bond the powder particles and densify the bond coat layer 16a. The heat treatment also preferably diffusion bonds the layer 16a to the substrate 12. A preferred treatment is a temperature of about 950 C to about 1150 C and a duration of about one to about six hours in a vacuum or inert atmosphere. The bond coat layer 16a is also preferably degreased to remove all dirt, grease and other potential contaminants.

The APS bond coat layer 16b is then deposited on the HVOF bond coat layer 16a using the above-described process and powder. The preferred APS powder described above contains a sufficient amount of coarser particles to produce an adequate surface macro-roughness for the bond coat 16, and a sufficient amount of finer particles to yield an adequate surface micro-roughness for adhesion of the ceramic layer 18 and also fill the interstices between the coarser particles to increase the density of the APS bond coat layer 16b. According to this invention, the resulting bond coat 16 has a surface roughness of about 350 microinches to about 750 microinches (about 9 to about 19 m) Ra. Prior to exposure to a high-temperature oxidizing environment, the bond coat layer 16b is also subjected to a heat treatment sufficient to diffusion bond the APS bond coat layer 16b to the HVOF bond coat layer 16a. A preferred treatment is a temperature of about 950 C to about 1150 C and a duration of about

- 10 -

one to about six hours in a vacuum or inert atmosphere, and yields a coating density of at least about 95% of theoretical (i.e., porosity of not more than 5%). A suitable thickness for the APS bond coat layer 16b is about 100 to about 300 micrometers.

5 During an investigation of this invention, bi-layer bond coats in accordance with this invention were comparatively tested against prior art VPS bond coats. The substrate material for all specimens was a nickel-base superalloy having a nominal composition, in weight percent, of 14 Cr, 9.5 Co, 3 Al, 4.9 Ti, 1.5 Mo, 10 3.8 W, 2.8 Ta, 0.010 C, balance Ni and incidental impurities. The bond coat composition for all specimens was the NiCrAlY material described above, having a nominal composition, in weight percent, of about 22% chromium, about 10% aluminum, about 1% yttrium, the balance nickel and incidental impurities. The HVOF and APS bond coat layers of this 15 invention were deposited from powders having the preferred particle size distributions stated above, while the powder deposited by VPS had a particle size range of about 10 to about 90 m. The HVOF process parameters included a hydrogen gas flow of about 1600 standard cubic feet per hour (scfh), an oxygen gas flow of about 450 20 scfh, a nitrogen gas flow of about 800 scfh, and a carrier (nitrogen) gas flow of about 30 scfh. The APS process parameters included a nitrogen gas flow of about 125 scfh, a hydrogen gas flow of about 9 scfh, and a carrier (nitrogen) gas flow of about 20 scfh (two injectors, 10 scfh per injector). The HVOF and APS bond coat layers had 25 thicknesses of about 200 and about 100 m, respectively, while the VPS bond coats had thicknesses of about 300 m. All specimens were heat treated at about 1080 C for a duration of about four hours in a vacuum after each deposition step. Following heat treatment, the bond coats of this invention were characterized by a surface roughness of about 450 30 to 600 microinches Ra and a density (APS layer) of about 98% of theoretical, while the VPS bond coats were characterized by a surface roughness of about 450 to 600 microinches Ra and a density of about 99% of theoretical.

- 11 -

Following deposition on all specimens of a thermal-insulating ceramic layer having a thickness of about 375 m, furnace testing was performed. Some of the specimens were subjected to thermal cycle testing that consisted of 45 minute cycles at about 2000 F (about 1095 C) over a 20-hour period, by which spallation resistance of the ceramic layer was evidenced by the number of thermal cycles survived before spallation. A second test entailed subjecting specimens to 2000 F for 1000 hours, by which depletion of aluminum in the substrate was determined by post-test examination. The results of the furnace tests are summarized below.

Specimens	Cycles to 1000 hrs.	
	Spallation	@2000°F
HVOF/APS bond coat	65	6%
VPS bond coat	58	0

The above data evidence the superiority of the HVOF/APS bond coats produced by this invention over the prior art VPS bond coats in terms of spallation resistance. Post-test examination showed some depletion of the aluminum in the superalloy substrates protected by the HVOF/APS bond coats near the bond coat-substrate interface. While the superalloy substrates protected by the VPS bond coats did not exhibit aluminum depletion, the trade-off was a shorter thermal cycle fatigue life.

While the invention has been described in terms of a preferred embodiment, it is apparent that other forms could be adopted by one skilled in the art, such as by substituting other materials for the substrate, bond coat layers and thermal-insulating layers of the coating system, or forming the bond coat to contain multiple HVOF and/or APS bond coat layers. Therefore, the scope of the invention is to be limited only by the following claims.

- 12 -

What is claimed is:

1. A method of depositing a bi-layer bond coat 16 of a thermal barrier coating system 14, the method comprising the steps of:

providing a superalloy substrate 12;

5 depositing a first bond coat layer 16a on the substrate 12 by an high velocity oxy-fuel technique using a first metallic powder of particles having a maximum size of 55 micrometers, the first bond coat layer 16a having a surface roughness of about 200 to about 400 microinches Ra;

10 prior to exposure to a high-temperature oxidizing environment, heat treating the first bond coat layer 16a in a vacuum or inert atmosphere to densify the first bond coat layer 16a and diffusion bond the particles of the first metallic powder;

15 depositing a second bond coat layer 16a on the first bond coat layer 16a by air plasma spraying a second metallic powder of particles having a size from about 35 to about 110 micrometers, the second bond coat layer 16a having a porosity of less than 5% and a surface roughness of about 450 to about 750 microinches Ra that is attributable to larger particles of the second metallic powder; and

20 prior to exposure to a high-temperature oxidizing environment, heat treating the first 16a and second bond coat 16b layers in a vacuum or inert atmosphere to diffusion bond the second bond coat layer 16b to the first bond coat layer 16a.

2. A method as recited in claim 1, wherein the first metallic powder is formed of an oxide scale-forming composition.

3. A method as recited in claim 1, wherein the second metallic powder is formed of an oxide scale-forming composition.

4. A method as recited in claim 1, wherein the first and second metallic powders are formed of oxide scale-forming metal

- 13 -

- compositions selected from the group consisting of aluminum-containing intermetallics, chromium-containing intermetallics, MCrAl, where M equals iron, nickel and/or cobalt, MCrAlY, where M equals iron, nickel and/or cobalt, and combinations thereof.
- 5

5. A method as recited in claim 1, wherein the first metallic powder has a particle size distribution of, in weight percent, about 19% particles from 44 to 55 m, about 42% particles from 31 to 44 m, about 31% particles from 22 to 31 m, and about 5% particles from 16 to 22 m, and wherein the second metallic powder has a particle size distribution of, in weight percent, about 5% particles from 75 to 90 m, about 25% particles from 63 to 75 m, about 50% particles from 53 to 63 m, about 15% particles from 45 to 53 m, and about 5% particles from 38 to 45 m.
- 5

6. A method as recited in claim 1, further comprising the step of degreasing the first bond coat layer 16a prior to depositing the second bond coat layer 16b.

7. A method as recited in claim 1, wherein the step of heat treating the first bond coat layer 16a causes the first metallic powder to diffusion bond to the substrate 12.

8. A method as recited in claim 1, further comprising the step of depositing a thermal-insulating layer 18 on the second bond coat layer 16b.

9. A method as recited in claim 1, wherein the substrate 12 is formed of a nickel-base superalloy.

10. The thermal barrier coating system 14 formed by the method recited in claim 1.

11. A method of depositing a thermal barrier coating system 14, the method comprising the steps of:

providing a nickel-base superalloy substrate 12;

- 14 -

5 depositing a first bond coat layer 16a on the substrate 12 by an HVOF technique using a first metallic powder of particles having a size of about 20 to about 55 micrometers, the first bond coat layer having a surface roughness of about 200 to about 400 microinches Ra;

10 prior to exposure to a high-temperature oxidizing environment, heat treating the first bond coat layer 16a in a vacuum or inert atmosphere to densify the first bond coat layer 16a, diffusion bond the particles of the first metallic powder, and diffusion bond the first metallic powder to the substrate 12;

15 depositing a second bond coat layer 16b on the first bond coat layer 16a by air plasma spraying a second metallic powder of particles having a size of from about 35 to about 110 micrometers, the second bond 16b coat layer having a porosity of less than 5% and a surface roughness of about 450 to about 750 microinches Ra that is attributable to larger particles of the second metallic powder;

20 prior to exposure to a high-temperature oxidizing environment, heat treating the first 16a and second bond coat 16b layers in a vacuum or inert atmosphere to diffusion bond the second bond coat layer 16b to the first bond coat layer 16a; and

depositing a thermal-insulating layer 18 on the second bond coat layer 16b by air plasma spraying.

12. A method as recited in claim 11, wherein the first metallic powder is formed of an oxide scale-forming composition.

13. A method as recited in claim 11, wherein the second metallic powder is formed of an oxide scale-forming composition.

5 14. A method as recited in claim 11, wherein the first and second metallic powders are formed of oxide scale-forming metal compositions selected from the group consisting of aluminum-containing intermetallics, chromium-containing intermetallics, MCrAl, MCrAlY, and combinations thereof.

- 15 -

15. A method as recited in claim 11, wherein the first and second metallic powders each have nominal compositions, in weight percent, of about 22% chromium, about 10% aluminum, about 1% yttrium, the balance nickel and incidental impurities.

16. A method as recited in claim 11, further comprising the step of degreasing the first bond coat layer 16a prior to depositing the second bond coat layer 16b.

17. A method as recited in claim 11, wherein the substrate 12 is formed of a nickel-base superalloy having a nominal composition, in weight percent, of 14 Cr, 9.5 Co, 3 Al, 4.9 Ti, 1.5 Mo, 3.8 W, 2.8 Ta, 0.010 C, balance Ni and incidental impurities.

18. The thermal barrier coating system formed by the method recited in claim 11.

19. A method of depositing a thermal barrier coating system 14, the method comprising the steps of:

providing a nickel-base superalloy substrate 12;

depositing a first bond coat layer 16a on the substrate 12
5 by an HVOF technique using a first metallic powder of particles having a size distribution of, in weight percent, about 19% particles from 44 to 55 m, about 42% particles from 31 to 44 m, about 31% particles from 22 to 31 m, and about 5% particles from 16 to 22 m, the first metallic powder being formed of an oxide scale-forming metal composition
10 selected from the group consisting of aluminum-containing intermetallics, chromium-containing intermetallics, MCrAl, MCrAlY, and combinations thereof, the first bond coat layer 16a having a surface roughness of about 200 to about 400 microinches Ra;

prior to exposure to a high-temperature oxidizing
15 environment, heat treating the first bond coat layer 16a in a vacuum or inert atmosphere at a temperature of about 950 C to about 1150 C for a duration of about one to about six hours to reduce the porosity of the

- 16 -

first bond coat layer 16a to less than 1%, diffusion bond the particles of the first metallic powder, and diffusion bond the first metallic powder to the substrate 12;

degreasing the first bond coat layer 16a;

depositing a second bond coat layer 16b on the first bond coat layer 16a by air plasma spraying a second metallic powder of particles having a size distribution of, in weight percent, about 5% particles from 75 to 90 m, about 25% particles from 63 to 75 m, about 50% particles from 53 to 63 m, about 15% particles from 45 to 53 m, and about 5% particles from 38 to 45 m, the second metallic powder being formed of an oxide scale-forming metal composition selected from the group consisting of aluminum-containing intermetallics, chromium-containing intermetallics, MCrAl, MCrAlY, and combinations thereof, the second bond coat layer having a porosity of less than 5% and a surface roughness of about 450 to about 750 microinches Ra that is attributable to larger particles of the second metallic powder;

prior to exposure to a high-temperature oxidizing environment, heat treating the first 16a and second bond coat layers 16b in a vacuum or inert atmosphere at a temperature of about 950 C to about 1150 C for a duration of about one to about six hours to diffusion bond the second bond coat layer 16b to the first bond coat layer 16a; and

depositing a thermal-insulating layer 18 on the second bond coat layer 16b by air plasma spraying.

20. The thermal barrier coating system 14 formed by the method recited in claim 19.

21. A bi-layer bond coat 16 comprising:

a first bond coat layer 16a using a first metallic powder of particles having a maximum size of 55 micrometers, the first bond coat layer 16a having a surface roughness of about 200 to about 400 microinches Ra; and

- 17 -

a second bond coat layer 16b on the first bond coat layer 16a using a second metallic powder of particles having a size from about 35 to about 110 micrometers, the second bond coat layer 16b having a surface roughness of about 450 to about 750 microinches Ra.

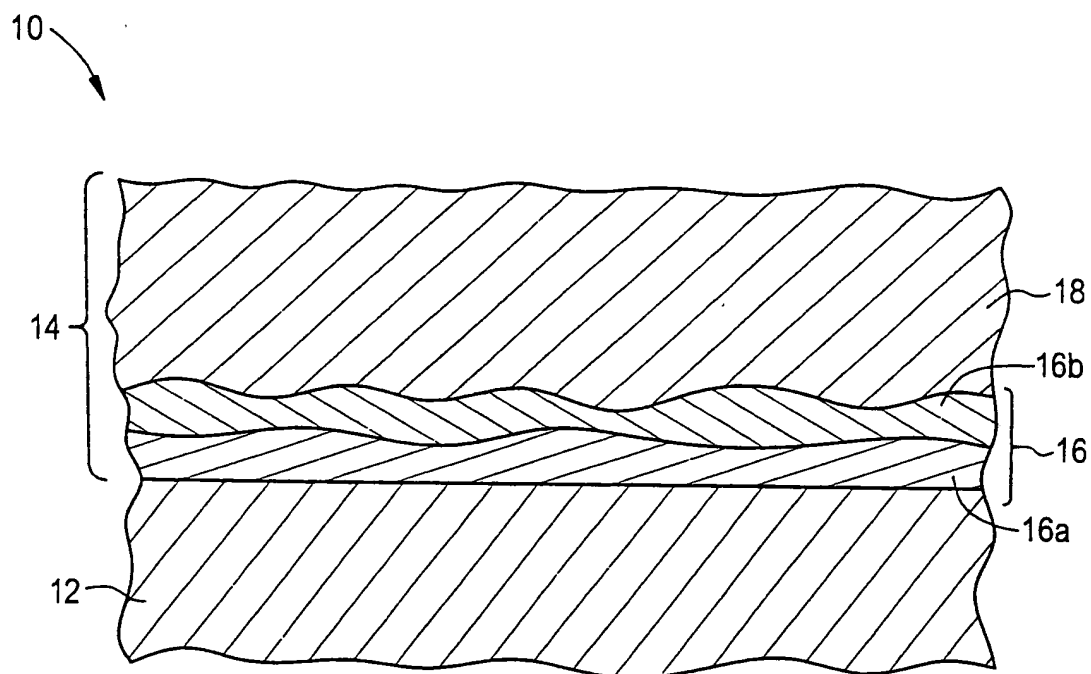
22. A bi-layer bond coat 16 as recited in claim 21 where the first metallic powder is an oxide scale-forming composition.

23. A bi-layer bond coat 16 as recited in claim 21 where the second metallic powder is an oxide scale-forming composition.

24. A bi-layer bond coat 16 as recited in claim 21 where the first and second metallic powders are formed of compositions selected from the group consisting of aluminum-containing intermetallics; chromium-containing intermetallics; MCrAl, where M equals iron, nickel and/or cobalt; MCrAY, where M equals iron, nickel and/or cobalt; and mixtures thereof.

25. A bi-layer bond coat 16 as recited in claim 21 where the first metallic powder has a particle size distribution of, in weight percent, about 19% particles from 44 to 55 m, about 42% particles from 31 to 44 m, about 31% particles from 22 to 31 m, and about 5% particles from 16 to about 22 m and where the second metallic powder has a particle size distribution of, in weight percent, about 5% particles from 75 to 90 m, about 25% particles from 63 to 75 m, about 50% particles from 53 to 63 m, about 15% particles from 45 to 53 m, and about 5% particles from 38 to 45 m.

FIG. 1



INTERNATIONAL SEARCH REPORT

Inter Application No
PCT/US 99/04339

A. CLASSIFICATION OF SUBJECT MATTER
IPC 6 C23C4/02 C23C28/00

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 6 C23C

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 5 579 534 A (ITOH MASAYUKI ET AL) 26 November 1996	1-4, 7-15, 18, 21-24
A	see abstract; figures 1,3 see column 1, line 6 - line 8 see column 2, line 30 - line 38 see column 2, line 51 - line 67 see column 3, line 22 - column 4, line 51 see column 5, line 16 - line 51 see column 6, line 20 - line 35 see claims 1,3,6,8,9,19,20; examples 1,2 --- -/--	5, 17, 19, 20, 25

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

* Special categories of cited documents :

- "A" document defining the general state of the art which is not considered to be of particular relevance
- "E" earlier document but published on or after the international filing date
- "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- "O" document referring to an oral disclosure, use, exhibition or other means
- "P" document published prior to the international filing date but later than the priority date claimed

- "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.
- "&" document member of the same patent family

Date of the actual completion of the international search

11 June 1999

Date of mailing of the international search report

23/06/1999

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

Ceulemans, J

INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 99/04339

C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y	US 4 095 003 A (WEATHERLY MERLE HOWARD ET AL) 13 June 1978	1-4, 7-15, 18, 21-24
A	see abstract see column 1, line 5 - line 10 see column 2, line 18 - column 3, line 57 see column 4, line 1 - line 21 see column 5, line 16 - line 24 see claims 1-4, 6	17, 19, 20
Y	EP 0 814 178 A (CHROMALLOY UK LTD ;ROLLS ROYCE PLC (GB)) 29 December 1997	1-4, 7-15, 18, 21-24
A	see abstract see column 1, line 2 - line 6 see column 2, line 47 - column 3, line 28 see column 4, line 16 - column 5, line 6 see column 5, line 53 - column 7, line 4 see claims 1, 2, 4-8, 10, 12-14, 23-26; figures	6, 16, 19
A	PATENT ABSTRACTS OF JAPAN vol. 018, no. 040 (C-1155), 21 January 1994 & JP 05 263212 A (TOSHIBA CORP), 12 October 1993 see abstract	1, 11, 19, 21
A	EP 0 532 255 A (GEN ELECTRIC) 17 March 1993 see the whole document	1-25

INTERNATIONAL SEARCH REPORT

Information on patent family members

Inter Application No

PCT/US 99/04339

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US 5579534 A	26-11-1996	JP 8041619 A	13-02-1996
US 4095003 A	13-06-1978	BE 858532 A	08-03-1978
		CA 1095342 A	10-02-1981
		CH 623607 A	15-06-1981
		DE 2740398 A	16-03-1978
		FR 2364276 A	07-04-1978
		GB 1588984 A	07-05-1981
		JP 1093308 C	16-04-1982
		JP 53033931 A	30-03-1978
		JP 56039389 B	12-09-1981
EP 0814178 A	29-12-1997	AU 2486097 A	08-01-1998
		CA 2208389 A	19-12-1997
		JP 10121264 A	12-05-1998
EP 0532255 A	17-03-1993	US 5236745 A	17-08-1993
		CA 2076118 A	14-03-1993
		JP 5195188 A	03-08-1993
		US 5403669 A	04-04-1995

THIS PAGE BLANK (USPTO)